

# A possible new family of unconventional high temperature superconductors

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We suggest a new family of Co/Ni-based materials that may host unconventional high temperature superconductivity (high- $T_c$ ). These materials carry layered square lattices with each layer being formed by vertex-shared transition metal tetrahedra cation-anion complexes. The electronic physics in these materials is determined by the two dimensional layer and is fully attributed to the three near degenerated  $t_{2g}$  d-orbitals close to a  $d^7$  filling configuration in the d-shell of Co/Ni atoms. The electronic structure meets the necessary criteria for unconventional high  $T_c$  materials proposed recently by us to unify the two known high- $T_c$  families, cuprates and iron-based superconductors. We predict that they host superconducting states with a d-wave pairing symmetry with  $T_c$  potentially higher than those of iron-based superconductors. These materials, if realized, can be a fertile new ground to study strongly correlated electronic physics and provide decisive evidence for superconducting pairing mechanism.

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Successful theoretical predictions of high temperature superconducting materials rarely happen. The two known families of high  $T_c$  materials, cuprates<sup>1</sup> and iron-based superconductors<sup>2</sup>, were discovered accidentally without any theoretical guide. Theoretical studies have been mainly devoted to explain rich phenomena observed in experiments. After almost three decades of intensive research, it has become extremely clear that if there is any chance to solve the elusive high  $T_c$  mechanism, a successful theoretical prediction of new high  $T_c$  materials is necessary.

Recently, we suggest that a special electronic trait that separates the two high  $T_c$  families from other correlated electronic materials is that in both high  $T_c$  families, those d-orbitals that make the strongest in-plane d-p couplings in the cation-anion complexes are isolated near Fermi surface energy<sup>3-5</sup>. In magnetically-driven superconducting mechanism, this property makes the effective antiferromagnetic (AFM) superexchange interactions to maximize their contribution to superconducting pairing and simultaneously reduces other unwanted side effects from other orbitals. We also further argued that this property can only be realized in very limited special cases<sup>4</sup>. Realizing such a property requires a strict symmetry match between local building blocks and global lattices, as well as a specific electron filling configuration in the d-shells of transition metal atoms. In cuprates, which possess perovskite or perovskite-like structures, the speciality is only realized near the  $d^9$  filling configuration in an octahedra (or square) complex to isolate the  $e_g$   $d_{x^2-y^2}$  orbital near Fermi energy. In iron-based superconductors, it is only realized near the  $d^6$  filling configuration of a tetrahedra complex to isolate two  $t_{2g}$   $d_{xy}$ -type orbitals<sup>3,4</sup>. Therefore, this speciality allows us to explain why high  $T_c$  is such a rare phenomenon. It can be considered as a gene type character to guide us to search for or predict possible new high  $T_c$  materials<sup>3</sup>.

Following the above analysis, we have predicted that the gene exists in a two dimensional hexagonal lattice formed by edge-shared trigonal bipyramidal complexes with a  $d^7$  electron filling configuration, which suggests that  $\text{Co}^{2+}/\text{Ni}^{3+}$

based materials containing this type of hexagonal lattices are promising new high  $T_c$  materials<sup>3</sup>. However, confirming such a prediction can be very difficult due to the rare appearance of trigonal bipyramidal complexes in material databases.

Here we propose a new family of Co/Ni-based materials that carry the special electronic property to be promising unconventional high- $T_c$  candidates. The materials are constructed by layered square lattices with each layer being formed by vertex-shared tetrahedra cation-anion complexes. When it is close to the  $d^7$  filling configurations in the d-shell, namely those of  $\text{Co}^{2+}$  or  $\text{Ni}^{3+}$ , the electronic physics in these materials are fully attributed to the three near degenerated  $t_{2g}$  d-orbitals. The new materials closely resemble both cuprates and iron-based superconductors, and thus can bridge the gap between their electronic properties. In fact, we predict that the materials have the same d-wave pairing symmetry in superconducting states as cuprates and can reach a maximum  $T_c$  higher than those of iron-based superconductors. The new family of materials, if synthesized, can be a fertile new ground to study strongly correlated electronic physics and test various ideas on both cuprates and iron-based superconductors.

Our proposal is deeply related to iron-based superconductors. Therefore, we first review the electronic structures of iron-based superconductors. In iron-pnictides, as shown in Fig.1(a), the two dimensional FeAs layer is constructed by edge sharing between two nearest neighbour (NN)  $\text{FeAs}_4$  tetrahedra complexes. As explicitly pointed out before<sup>3,4,6</sup>, the edge sharing between two sublattices has a profound effect on electronic structures of iron-pnictides. It makes one combination of  $d_{xz}$  and  $d_{yz}$  orbitals noted as  $d_{xz/yz}^{**}$  strongly couples with the  $e_g$   $d_{x^2-y^2}$  orbital. Such a coupling creates an energy gap between their binding and antibinding bands to allow the  $d_{xy}$  and the other combination of  $d_{xz}$  and  $d_{yz}$  orbital noted as  $d_{xz/yz}^*$ , the two pure  $t_{2g}$  orbitals, separated from all other d-orbitals. As shown in Fig.1(a), the  $d^6$  filling configuration makes these two pure  $t_{2g}$  orbitals isolated near Fermi energy, which explains why  $\text{Fe}^{2+}$  is specially required to realize high  $T_c$  in iron-based superconductors<sup>4</sup>. In this analysis, the su-

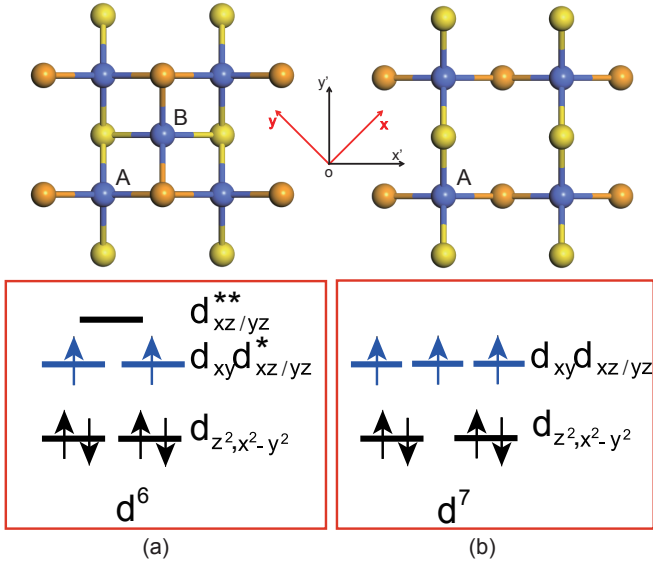


FIG. 1: (color online) The two dimensional layer structures, the corresponding d-orbital crystal energy splitting configurations and the required electron filling configuration to realize high temperature superconductivity: (a) a FeAs(Se) layer in iron-based superconductors with the  $d^6$  filling configuration; (b) the proposed layer by keeping only cation atoms at the A sublattice of (a) with the  $d^7$  filling configuration.

perconducting pairing essentially is confined between two  $t_{2g}$  orbitals within each sublattice.

Following the above understanding of iron-based superconductors, logically we can simply keep one Fe sublattice without losing essential physics. If we divide Fe atoms into two sublattices, each sublattice as shown in Fig. 1(b) can be viewed as a structure constructed by vertex sharing between two NN tetrahedra. Thus a natural proposal is to study a material which has a lattice structure of Fig. 1(b). This is exactly the main point of this paper. It is easy to notice that in this lattice there is no large coupling between  $e_g$  and  $t_{2g}$  orbitals. The  $e_g$  and  $t_{2g}$  orbitals are well separated in energy by crystal field energy splitting. All three  $t_{2g}$  orbitals are close to be degenerated. Therefore, as shown in Fig. 1(b), a configuration close to a  $d^7$  filling on transition metal ion meets the requirements to isolate the  $t_{2g}$  orbitals near Fermi energy. Thus, our goal is to construct  $Co^{2+}$  or  $Ni^{3+}$  based materials containing such a two dimensional lattice structure and predict possible properties.

The first question is that whether the lattice structure in Fig. 1(b) is feasible or not. The answer is positive. In fact, the layer structure exists in the popular zinc blende structure ( $\beta$ -ZnS). As shown in Fig. 2(a), the zinc blende is a well known three dimensional cubic structure created by vertex-sharing tetrahedra. If we view the cubic structure layer by layer along any principle axis, each  $ZnS_2$  layer is identical to the structure shown in Fig. 1(b). For the purpose of theoretical demonstration, we can replace half Zn atoms in  $ZnS$  by Co atoms to create a prototype of material  $ZnCoS_2$  that has alternating  $ZnS_2$  and  $CoS_2$  layers along c-axis, shown in Fig. 2(b). We can also make extension of this material by replacing S

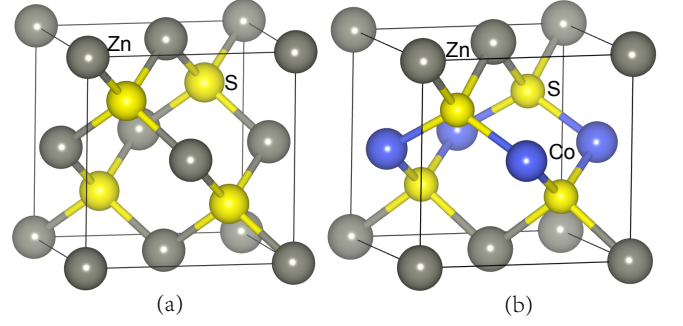


FIG. 2: (color online) (a) the ZnS(Sphalerite) Zinc Blende structure; (b) a possible  $ZnCoS_2$  structure with alternating Zn and Co layers.

TABLE I: Optimized structural parameters of  $ZnCoS_2$  and  $ZnCoSe_2$  by using GGA .

	$ZnCoS_2$	$ZnCoSe_2$
$a(\text{\AA})$	3.757	3.758
$c(\text{\AA})$	5.017	6.000
Co-Se(S)( $\text{\AA}$ )	2.172	2.319
Se(S)-Co-Se(S)	$119.757^\circ; 104.586^\circ$	$108.204^\circ; 110.109^\circ$

atoms by other chalcogen atoms to create materials such as  $ZnCoO_2$  and  $ZnCoSe_2$ . However, for  $ZnCoO_2$ , we find that the lattice constant is only about  $3.1\text{\AA}$ , much smaller than those of  $ZnCo(S,Se)_2$ . The short distance suggests that there are strong direct hoppings between d-orbitals which can destroy the superexchange processes. Therefore, we will focus on  $ZnCo(S,Se)_2$ . In these materials, the electronic physics near Fermi energy is expected to be dominated by the two dimensional Co(S,Se)<sub>2</sub> layer as Zn has a filled d-shell.

We use the density functional theory (DFT) under the generalized-gradient approximation (GGA) for the exchange correlation functional<sup>7-10</sup> to obtain the optimized structural parameters for both  $ZnCo(S,Se)_2$  which are listed in Table I.  $CoSe_4$  is close to a perfect tetrahedra. S atoms in  $ZnCoS_2$  are much closer to Co layer than Se atoms in  $ZnCoSe_2$ . These lattice differences are consistent with those between FeS and FeSe in iron-based superconductors<sup>11</sup>. The band structures of these two materials are shown in Fig. 3 in which different colors mark the orbital characters. It is very clearly that the three  $t_{2g}$  orbitals are close to half filling and dominate the electronic physics near Fermi energy. The dispersions along c-axis are not small, which suggests that there are reasonable couplings between two NN Co layers. This is largely because of the cubic nature of the original Zinc Blende structure. In principle, we may design a material to make large separations between NN Co layers to reduce the c-axis dispersion. For example, in iron-based superconductors, the c-axis dispersion of the 1111 LaOFeAs is much weaker than those of the 122 BaFe<sub>2</sub>As<sub>2</sub> and the maximum  $T_c$  is higher in the former than the latter<sup>12</sup>. Therefore, the large c-axis dispersion here is clearly not good for achieving maximum  $T_c$ , which suggests  $ZnCo(S,Se)_2$  may be not the optimal materials to achieve the maximum potential  $T_c$  in these families. Nevertheless, the es-

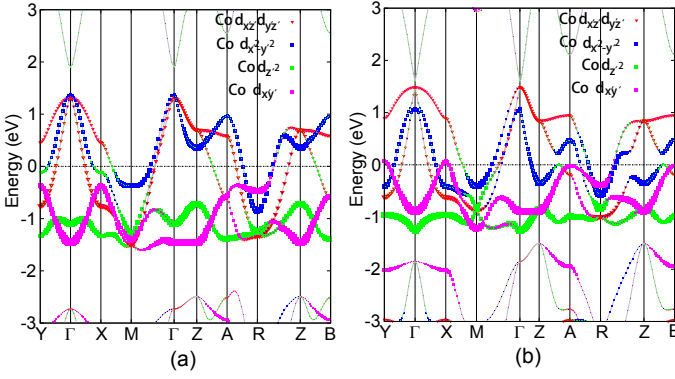


FIG. 3: (color online) (a) and (b) are band structures of ZnCoS<sub>2</sub> and ZnCoSe<sub>2</sub>. The orbital characters of bands are represented by different colors.

sential two dimensional physics from the Co(S,Se)<sub>2</sub> layer can still be analyzed in this prototype by focusing on a single two dimensional layer.

The minimum effective tight binding model Hamiltonian  $H_0$  to capture the three  $t_{2g}$  orbitals near Fermi surfaces in a single layer can be written as a  $3 \times 3$  Hermitian matrix. In the following, we use the two principle axes of the Co square lattice,  $x'$  and  $y'$  as shown in Fig. 1 and take the  $t_{2g}$  orbital base ( $d_{x'z}$ ,  $d_{y'z}$ ,  $d_{x'^2-y'^2}$ ). Without causing confusion, we ignore the prime label in the following of the paper. The elements of  $H_0$  matrix are given by

$$\begin{aligned} H_{11} &= \epsilon_1 + 2t_x^{11}\cos(k_x) + 2t_y^{11}\cos(k_y) + 4t_{xy}^{11}\cos(k_x)\cos(k_y) \\ &\quad + 2t_{xx}^{11}\cos(2k_x) + 2t_{yy}^{11}\cos(2k_y), \\ H_{12} &= -4t_{xy}^{12}\sin(k_x)\sin(k_y) \\ H_{13} &= 2it_x^{13}\sin(k_x) + 4it_{xy}^{13}\sin(k_x)\cos(k_y) + 2it_{xx}^{13}\sin(2k_x) \\ H_{22} &= \epsilon_2 + 2t_x^{22}\cos(k_x) + 2t_y^{22}\cos(k_y) + 4t_{xy}^{22}\cos(k_x)\cos(k_y) \\ &\quad + 2t_{xx}^{22}\cos(2k_x) + 2t_{yy}^{22}\cos(2k_y), \\ H_{23} &= 2it_y^{23}\sin(k_y) + 4it_{xy}^{23}\sin(k_y)\cos(k_x) + 2it_{xx}^{23}\sin(2k_y) \\ H_{33} &= \epsilon_3 + 2t_x^{33}(\cos(k_x) + \cos(k_y)) + 4t_{xy}^{33}\cos(k_x)\cos(k_y) \\ &\quad + 2t_{xx}^{33}(\cos(2k_x) + \cos(2k_y)) \end{aligned} \quad (1)$$

We use eV as the energy unit for all parameters without further specification. By fitting to the band structure of ZnCoS<sub>2</sub> at the  $k_z = 0$  plane, we have  $\epsilon_1 = \epsilon_2 = 3.7314$  and  $\epsilon_3 = 4.1241$  for the onset energy of  $d_{xz,yz}$  and  $d_{x^2-y^2}$ . The corresponding hopping parameters in above equation are  $t_x^{11} = t_y^{22} = 0.4391$ ,  $t_y^{11} = t_x^{22} = 0.1408$ ,  $t_{xy}^{11} = t_{xy}^{11} = -0.0162$ ,  $t_{xy}^{12} = 0.021$ ,  $t_x^{13} = t_y^{23} = 0.0057$ ,  $t_{xy}^{13} = t_{xy}^{13} = -0.0061$ ,  $t_{xx}^{33} = 0.1824$ ,  $t_{xy}^{33} = 0.011$ ,  $t_{xx}^{11} = t_{yy}^{22} = 0.0688$ ,  $t_{yy}^{11} = t_{xx}^{22} = -0.0025$ ,  $t_{xx}^{13} = t_{yy}^{23} = 0.0107$ ,  $t_{xx}^{33} = -0.0299$ . It is clear that the hoppings are dominated by the NN intra-orbital hoppings. The positive values of these hopping parameters reflect that the hoppings are mediated through the p-orbitals of S/Se anions. The Fermi surfaces and the band structure with these parameters are shown in Fig. 4. The Fermi surfaces are composed of two large hole pockets around  $\Gamma$  and one large

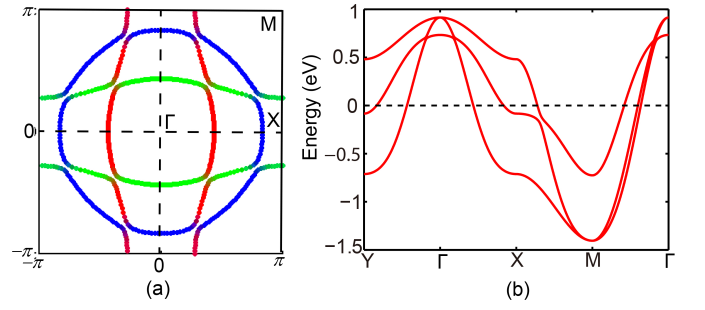


FIG. 4: (color online) (a) The Fermi surface of ZnCoS<sub>2</sub>. The orbital contributions of the different FS sheets are shown color coded:  $d_{xz}$  (green),  $d_{yz}$  (red) and  $d_{xy}$  (blue). (b) The band structure of the effective model.

electron pockets around  $M$ .

Similar to cuprates, here we expect that the electron-electron correlation can be described effectively by onsite interactions. In this multi-orbital system it can be written as  $H_{eff} = \sum_i H_i$  with

$$H_i = \sum_a U n_{ia\uparrow} n_{ia\downarrow} + \sum_{\langle ab \rangle} (U' n_{ia} n_{ib} - J_H \vec{S}_{ia} \cdot \vec{S}_{ib}), \quad (2)$$

where the terms represent the Hubbard intra-orbital repulsion, inter-orbital repulsion and Hunds coupling respectively, and  $a, b$  are orbital indices. Near half filling, as the magnetism is controlled by the AFM superexchanges, the effective Hamiltonian for effective spin-spin interactions can be written as

$$H_s = \sum_{\langle ij \rangle} J_{ab} \vec{S}_{ia} \cdot \vec{S}_{jb}, \quad (3)$$

where  $\langle ij \rangle$  is defined between two NN sites.  $J_{ab}$  are expected to be dominated by intra-orbital AFM couplings, namely  $J_{a=b}$  are much larger than  $J_{a \neq b}$ . Combining  $H_0$  with these effective interactions provides a minimum model to describe the system.

In this paper, rather than solving above model quantitatively, here we are interested in robust qualitative predictions that can be made for this system based on general principles obtained from cuprates and iron-based superconductors<sup>4</sup>. Verifying these predictions can be a strong demonstration of these principles. In the following, several important issues are in order.

First, we find that the parental compounds of the new system can be a Mott insulator or, at least, is in the vicinity to the Mott insulating phase. The parental compounds of cuprates are Mott insulators but the iron-based superconductors are known to be metallic. These differences have led to many debates whether both materials can be understood in one category. The new family can serve a bridge to address this question. On one side, there are odd number of electrons in the current system, which is the same as the case in cuprates<sup>13</sup>. With the odd number, the Mott insulator concept is well defined. On the other side, the current multi-orbital system is built on the essential multi-orbital physics of iron-based superconductors. In Fig. 5, we report the GGA+U calculation

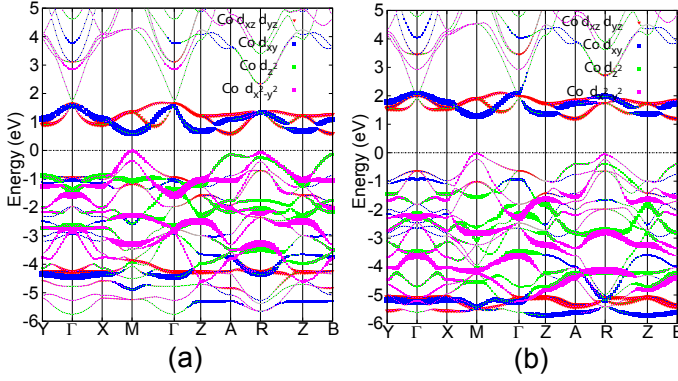


FIG. 5: The band structures under the GGA+U calculations for  $\text{ZnCoSe}_2$ : (a)  $U=2\text{eV}$ ; (b)  $U=4\text{eV}$ .

for  $\text{ZnCoSe}_2$ . The material has a G-type AFM ground state. The ordered magnetic moment is about  $1.76\mu_B$  without  $U$ ,  $2.14\mu_B$  at  $U = 2.0\text{eV}$  and  $2.37\mu_B$  at  $U = 4.0\text{eV}$ . The AFM ground state is metallic without  $U$ . However, they are insulating at both  $U = 2.0\text{eV}$  and  $U = 4.0\text{eV}$ . The insulating gap increases as  $U$  increases. These results are very similar to those from a similar calculation for cuprates and strongly imply for Mottness in this material.

Second, we predict that in this system, similar to cuprates, the pairing symmetry in the superconducting state is a robust d-wave pairing upon doping near half filling. Recently, one basic principle to unify the pairing symmetries in cuprates and iron-based superconductors was specified by Hu and Ding<sup>14</sup>: the pairing symmetry is simply selected by the overlap between the pairing form factors which are determined from the short range AFM exchange interactions and the Fermi surfaces. A large overlap is also a necessary condition to achieve high  $T_c$ . This principle, which we refer it as the *Hu-Ding* principle, was also generalized to include other orders later in ref.<sup>15</sup> by Davis and Lee. The principle provides an unified explanation why the d-wave pairing symmetry and the extended s-wave pairing symmetry are robust respectively in cuprates and iron-based superconductors<sup>5</sup>.

In the current system, as argued earlier, the AFM exchange couplings are dominated by the NN intra-orbital couplings which can generate NN intra-orbital pairing. For a d-wave, the pairing form factor for the  $d_{x^2-y^2}$  orbital is  $\cos k_x - \cos k_y$ . For the pairing form factors for the  $d_{xz}$  and  $d_{yz}$  orbitals are  $\cos k_x$  and  $-\cos k_y$  respectively. These form factors have a very large overlap to the Fermi surfaces shown in Fig.4. If we consider the extended s-wave, it is clear that there is little overlap between Fermi surfaces and the extended s-wave form factor  $\cos k_x + \cos k_y$  for  $d_{x^2-y^2}$  orbital. Therefore, following the Hu-Ding principle, the superconducting state should have a robust d-wave pairing symmetry upon doping near half filling.

Finally, we predict that the maximum  $T_c$  in these systems should be higher than the maximum  $T_c$  achieved in iron-based superconductors. The superconducting transition temperature can be affected by many factors. However, if the superconducting mechanism is assumed to be identical, we can com-

pare the maximum achievable  $T_c$  between different families based on their intrinsic energy scales. The ratio of the maximum  $T_c$ s observed in cuprates and iron-based superconductors is indeed roughly consistent with the energy scale ratio between two families<sup>3</sup>. In the current system, the energy scale is identical to those of iron-based superconductors. However, because here all  $t_{2g}$  orbitals participate in superconducting pairing, it is reasonable to argue that the maximum  $T_c$  should exceed those of iron-based superconductors where only two  $t_{2g}$  orbitals essentially make contribution to pairing.

It is interesting to notice that the band structures of our proposed systems are very similar to those of  $\text{Sr}_2\text{RuO}_4$  where there are 4 electron in three  $t_{2g}$  orbitals<sup>16</sup>. However, the physics between these two systems are rather different. The latter is clearly a weakly correlated electron system and the  $t_{2g}$  orbitals are very weakly connected to the surrounding p-orbitals of oxygens.

Our proposed systems can exhibit many unique properties. As the electronic structure is featured with three near degenerated orbitals. It is relatively easy to develop orbital orders. The electronic nematicity which exists in iron-based superconductors can also take place. Moreover, in this lattice structure, the bonding angle of Co-S(Se)-Co is relatively easy to be changed under pressure. Thus, many electronic properties can be very sensitive to external or internal pressure. Combining with Mottness physics, the intertwining physics between all these possible phenomena make this system an extremely intriguing system.

Upon a heavy electron doping, it is also possible that a superconducting state with a  $d \pm is$  pairing symmetry may develop because of the existence of the three  $t_{2g}$  orbitals. An extended s-wave for the  $d_{xz}$  and  $d_{yz}$  is very energetically competitive to the d-wave pairing symmetry based on the Hu-Ding principle, but not for the  $d_{x^2-y^2}$  orbital. Therefore, if the d-wave pairing on the  $d_{x^2-y^2}$  orbitals is weakened upon doping, it is possible to develop a  $d \pm is$  pairing symmetry in which the pairing symmetry within the  $d_{xz}$  and  $d_{yz}$  orbitals are an extended s-wave.

In the current material database, we have not found a Co or Ni-based bulk material that carries the proposed two dimensional layer structure. However, there are Co-based bulk materials with layered Co chains formed by vertex shared  $\text{CoSe}_4$ , such as  $\text{CsYbCoSe}_3$ <sup>17</sup>, in which the valence of the Co atoms are  $2+$ . The existence of such a stable structure suggests that the proposed structure is feasible. Furthermore, as the zinc blende structure is a very popular and stable structure, it may be also possible to realize the proposed layer structure as an interface between two zinc blende structure by molecular beam epitaxy(MBE) method<sup>18</sup>. Finally, although we have focused on S and Se anion atoms in this paper to demonstrate the essential idea, we can also try halogens or pnictogens to check the possibility to form such a desired electronic structure.

In summary, we suggest that a new Co or Ni-based two dimensional square lattice structure constructed by vertex-shared tetrahedra can realize unconventional high  $T_c$  when the electron filling configuration in the d-shell is close to  $d^7$ . The electronic physics is fully attributed to the three near degenerated  $t_{2g}$  d-orbitals and supports a robust d-wave pairing



symmetry. Confirming these predictions can settle the elusive high  $T_c$  mechanism regarding both cuprates and iron-based superconductors.

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